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EVALUATION OF SPACECRAFT TOXIC
GAS REMOVAL AGENTS

FINAL REPORT ON CONTRACT NAS 9-12360

To

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MANNED SPACECRAFT CENTER

Houston, Texas

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REPORT NO. 3005-F

ANALYTICAL RESEARCH LABORATORIES, INC.

Monrovia, California 91016

CONTRACT FULFILLMENT STATEMENT

This final report is submitted to National Aeronautics and Space Admin-
istration, Manned Spacecraft Center in completion of Contract NAS
9-12360. It describes the studies and analyses of the adsorption and
desorption of chemical components on activated charcoal used in the
Apollo breathing canisters.

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ABSTRACT

A study of the decomposition of various compounds adsorbed on charcoal was made, with a view toward providing a critical appraisal of previous data from charcoal adsorption studies.

It was found that thermal decomposition occurs at temperature lower than previously suspected during the charcoal stripping process. A discussion is presented dealing with the various types of reactions found. A rough, quantitative scheme for correction of previous analytical results is developed and presented.

FOREWORD

This study was conducted by the Analytical Research Laboratories, Inc., Monrovia, California under Contract NAS 9-12360 for the Manned Spacecraft Center, Houston, Texas. Mr. W. J. Rippstein of NASA was the technical monitor.

Project Manager for ARLI was Mr. N. W. Hultgren with overall review and consultation from Mr. M. L. Moberg. Mr. Hultgren performed mass spectrometric analyses and was responsible for data reduction, computer studies, and report preparation. Assisting in gas chromatography were Messrs. C. L. Deuel, H. C. Harper, and A. C. Bogaardt, while emission spectroscopic work was performed by Mr. K. Inouye.

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I.   INTRODUCTION

During the analyses of charcoal adsorbents on several previous contracts (References 1 - 4), a list of some 250 compounds has been established (Table 1) of substances that have been desorbed from charcoal at one time or another.   The problem is presented as to whether any of these compounds are "artifacts".   That is, have they been formed during the interval of time between the use of the charcoal as an adsorbent and the final analysis by gas chromatography and mass spectroscopy. During this period vapors have been adsorbed on the charcoal and exposed to the presence of other compounds either on or passing through the charcoal.   The vapors have been stripped in an operation which involves exposure to high vacuum for 1 hour and heat of about $200^\circ C$ for 45 minutes. There has been a possible spiking in the temperature profile that may rise to $240^\circ C$ for a few minutes.   The compounds are condensed in liquid nitrogen and diluted with helium before passing through the gas chromatograph column.   The purpose of this program is to determine, where possible, what changes have been produced on the composition of the original adsorbed gases.

II.   TECHNICAL DISCUSSION

A.   STRIPPING OF CHARCOAL

The major likely source of any changes is during the stripping process.   The standard stripping process as used on the Apollo charcoals has been to place 50 g. in a 200 ml. round-bottom flask placed in a Glas-Col 140 watt heating mantle.   The flask is connected to a vacuum system pumped by a mercury diffusion pump.   The gases desorbed from the charcoal are passed through a U-tube trap kept at dry ice temperatures to adsorb water, then through a Schultz trap at liquid nitrogen temperatures to adsorb the remaining condensables.   Previous experience has shown the Schultz trap to be effective and to adsorb nearly all of the condensables.   The dry ice

trap adsorbs most of the water, and a generally insignificant amount of the remaining condensables. The flask containing the charcoal sample is gradually opened to the vacuum system to avoid a too fast rush of gas through the traps.

The powerstat on the heating mantle is then turned on to 100 volts for 15 minutes and then reduced to 45 volts for 45 minutes while the desorbed gases are trapped. The temperature of the charcoal as measured through a thermometer well reaches about $210^{\circ}C$ and then decreases to about $190^{\circ}C$ where it stays, while the temperature of the heating mantle, as measured by a thermocouple rises to $240^{\circ}C$ and then decreases to $200^{\circ}C$ where it stays constant. It is not unlikely that portions of the charcoal nearest the heating mantle reach $240^{\circ}C$ while the bulk remains cooler.

In order to determine what possible metal catalysts could be present two samples of Type AC charcoal were ashed and analyzed by emission spectroscopy. One sample was ashed in a platinum crucible, and the other in a gold crucible. There was approximately 1.5% ash from each firing. Qualitative emission spectrographic analysis showed the expected common elements; Mg, Al, Ca, Fe, K, Na. The results are summarized in Table 2. The trace of gold in the gold crucible indicated some fusion with that container. The gold crucible was used because of the possibility of platinum contamination in the platinum crucible, and even trace quantity of platinum may well have provided the catalyst sought. No platinum was detected. The appearance of the charcoal ash was interesting in that it showed a possible nonhomogeneous nature of charcoal. Some charcoal granules provided a gray ash, some had a greenish cast, and others were off white. This color variation may also have been caused by differences in degree of oxidation in that continued ashing seemed to result in more off white coloration. The ash was blended before taking the emission spectrographic samples, so possible content variation was not determined.

B. DISPLACEMENT STRIPPING

In the effort to determine whether the observed decomposition of compounds was due to adsorption on the charcoal or due to the effects of heating, or to a combination of both, a technique was sought that would strip the charcoal without the application of heat. A modification of displacement stripping was the first technique attempted.

Classical displacement analyses essentially consist of placing a sample on one end of a suitable adsorbant column, then effecting separation by passing a carrier gas containing the vapor of a substance more strongly adsorbed than any of the components of the sample through the column. The strongly adsorbed displacement substance will then force the sample to move down stream to new adsorption sites, where the various fractions displace, in turn, the others less strongly adsorbed. In this manner, the components arrange themselves according to their order of increasing affinity to the adsorbant and eventually emerge in succession from the end of the column. This method obviously leaves the adsorbant saturated with the displacement substance.

Dr. C. S. G. Phillips of Merton College, Oxford University, long recognized as one of the leading authorities in chemistry and gas chromatography, has suggested, in private communications, that we might find a modification of displacement chromatography, as frequently employed in his laboratories, useful in stripping charcoal.

Dr. Phillips has suggested that the classical method be somewhat what modified. Instead of introducing the displacement substance with the carrier gas, he proposed the addition of a discrete quantity. The adsorption capacity of charcoal is greatly reduced at higher temperatures; therefore, this slug would be moved down the column by chasing it with a band of localized heat. The advantages of this system are that the contaminants removed would not be subjected to a thermal soak (only a narrow band of displacement material would be subjected to heat); rather they would be partially

separated and stripped from the charcoal. This would effectively concentrate some of the lower level compounds and permit greater reliability in compound separation and identity if these separate fractions were individually trapped and chromatographed. The charcoal would be left in a clean, zero state for further use.

If catalytic conversion of compounds should occur primarily during the thermal-vacuum desorption process then one of the most certain ways to distinguish between compounds present in the spacecraft atmosphere and those formed from the action of the charcoal would be to provide an adequate alternate stripping procedure which would suppress the catalysis. A comparison of the desorbates from the two methods would leave little doubt as to those compounds present in the spacecraft. For these reasons, efforts were directed toward developing the displacement analysis using a heated moving solvent zone.

The first hot solvent displacement apparatus consisted of a ring burner mounted on a screw drive system to allow vertical travel of the burner at a rate of 5 min/inch. In the center of the burner was a 14 inch length of 3/8 stainless steel tubing, which contained the charcoal to be desorbed. The upper end of this tubing was teed to a septum for injection of the displacement solvent and admission of nitrogen (or other selected) carrier. The lower end of the tubing led to a thermoconductivity detector, then to a cryogenic trap. To test the system, samples of acetone were injected at the top of the column into the carrier of nitrogen just below the ring burner, which then started descending the column, driving the acetone before it. Tests utilizing this vertically traveling flame did not produce definitive information. Acetone injections of up to 5 μl produced no noticeable change in response of the thermal conductivity detector at the end of the flame travel (at which time the acetone should have been eluted). Injections of the same amount of acetone in an unpacked column (without

charcoal) produced sharp, well-defined responses. Apparently the acetone peak was either broadened by the charcoal, or the acetone was not desorbed by the flame. After the flame (moving heat zone) stripping, the charcoal sample was transferred to a vacuum flask and desorbed on the vacuum rack in the standard manner. This charcoal appeared to be no more contaminated than charcoal stripped in a vacuum oven, with benzene constituting the major desorbate and acetone representing a minor fraction. Apparently the acetone was desorbed.

A sample of "as received" charcoal was divided. One portion was vacuum thermally stripped, and the other subjected to displacement stripping with chlorobenzene. The thermal-vacuum desorbate consisted of large quantities of many compounds (as expected), but the displacement strip indicated very little in the way of desorbate as monitored by the thermal conductivity detector.

To achieve more uniform heating with a localized heat zone, the vertical flame travel was replaced by a horizontal travelling electrical heater on an Heraeus combustion furnace. Several runs were made using a helium carrier with a thermocouple placed 1 1/2 inches from the exit of the tube. By plotting the temperature as a function of the heater position in its travel and varying the heater and travel speed, optimum conditions were determined to achieve the greatest temperature gradient with the least preliminary heating of the charcoal by conduction. The localized heat zone could be varied from $650^{\circ}C$, at maximum settings, to a low of $350^{\circ}C$. Again using chlorobenzene as the stripping agent, a sample of as received charcoal was stripped. The desorbates were collected in LN_2 then analyzed. Numerous trace quantities of material were found, with benzene, Freon 113, chloroform, and chlorobenzene being the only constituents present in significant quantity.

Results were not encouraging with this method of stripping. A relatively insensitive thermal conductivity detector coupled with limited

charcoal sample size is probably responsible for poor desorption detection. Optimization of stripping solvent quantity, heat, and rate of travel may well produce stripping nearer to ideal.

C.   THERMAL DECOMPOSITION

The results of stripping small quantities of compounds from charcoal at 180°C, parallel modes of thermal decomposition that have been reported to occur only at higher temperatures. The very stable compounds such as hydrocarbons show no appreciable change while esters and halogenated compounds form a mixture of products. Typical reactions are found to be dehydrogenation, dehydration, hydrolysis, dehalogenation and isomerization. These are described as follows:

1.   Dehydrogenation of Alcohols and Alkanes.

Alcohols, according to the literature are dehydrogenated in excellent yields on hot copper in the temperature range $200^{\circ} - 300^{\circ}$C. Molecular hydrogen is evolved and the products are aldehydes or ketones. Dehydrogenation of methanol in air over hot silver or copper is a standard method for making formaldehyde. The hydrogen is oxidized to water and provides enough heat to maintain the reaction. Tertiary alcohols do not lose H_2 but may lose H_2O if the temperature is sufficiently high. The name "aldehyde" comes from alcohol dehydrogenation.

At high temperatures it is known that hot activated charcoal dehydrogenates cyclopentanes to cyclopentadienes. It will also convert cyclic alkanes to aromatic compounds.

2.   Isomerization.

Isomerization, though not yet definitely encountered in this program is a possibility. For example, it has been reported that at room temperature an equal mixture of C_4H_{10} hydrocarbons becomes 4/1 isobutane/butane. This equilibrium occurs rapidly in contact with a catalyst

of aluminum chloride and hydrogen chloride at 27°C, and it is conceivable that similar reactions may occur on hot charcoal.

3.   Dehydration of Alcohols.

Dehydration of alcohols is a moderately common thermal reaction. The order of ease of removal of water is tertiary > secondary > primary. Generally, the hydrogen is removed from the carbon that is poorer in hydrogen. Thus 2-pentanol usually dehydrates to 2-pentene rather than 1-pentene.

$$CH_3CHOHCH_2CH_2CH_3 \longrightarrow CH_3CH = CHCH_2CH_3 + H_2O$$
$$\underrightarrow{\quad not \quad} CH_2 = CH - CH_2CH_2CH_3 + H_2O$$
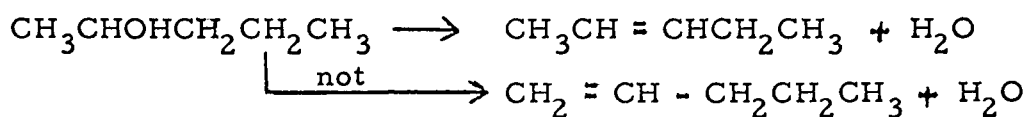
Dehydration of alcohols also is typically acid-catalyzed and rearrangements are common. The sulfuric acid dehydration product of n-butyl alcohol is 2-butene rather than the expected 1-butene. 2-butene is the thermodynamically more stable product. Also alkyl groups will frequently migrate within the structure as shown in the acid catalyzed dehydration below:
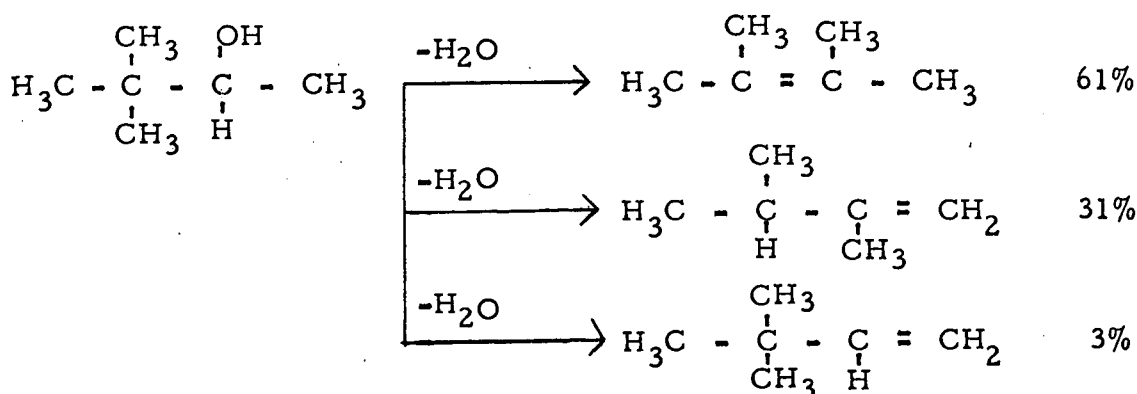
4.   Dehydrohalogenation.

When intramolecular degradation occurs, hydrogen and halogen atoms combine from neighboring atoms to form inorganic acids and an unsaturated organic product. Related to this degradation mechanism is straight dehalogenation. Probably when small amounts of moisture are present, a pair of neighboring halogen atoms combine and/ or are displaced from the structure and an unsaturated product is formed.

5.   Hydrolysis of Esters.

Esters are usually more thermally stable than their corresponding acids. However, the esterification reaction has a definite equilibrium between the alcohol, acid ester, and water. Under selected thermal conditions and probably charcoal catalytic acitvity, there should be some saponification of esters merely in the presence of water.

D.   DECOMPOSITION EXPERIMENTS WITH FREON 113

Halogenated compounds have been indicated as being the prime concern of the technical monitor. Freon 113 is used so extensively and is present in such large concentration in the charcoal desorbate, that its role as the principal halogen contributor must be considered. Essentially all of these adsorption-desorption efforts have produced the same results, with variations in operational parameters resulting only in differences in the extent of conversion, with essentially no differences in the compounds formed.

Freon 113 was found in this program to partially decompose to chlorotrifluoroethylene and dichlorodifluoroethylene. Partial decomposition of Freon 113 under these conditions has not been reported before, though the systhesis of chlorotrifluoroethylene from Freon 113 is of major commercial importance for the production of polychlorotrifluoroethylene.

Essentially, conversion of Freon 113 is accomplished by displacement of a molecule of chlorine to form the corresponding unsaturated compound. To a much lesser extent (averaging 2-3% of the total conversion)

CIF is displaced to form dichlorodifluoroethylene. Mechanisms by
which these conversions occur have not been verified, but possibly these
steps follow:

     1.   <u>Cis</u> - elimination from a four-membered ring transition
state as:

$$\underset{\underset{Cl\ \ Cl}{|\ \ \ |}}{\overset{\overset{F\ \ Cl}{|\ \ \ |}}{F-C-C-F}} \rightarrow \underset{}{\overset{\overset{F\ \ \ \ Cl}{|\ \ \ \ |}}{F-C = C-F}} + Cl_2$$
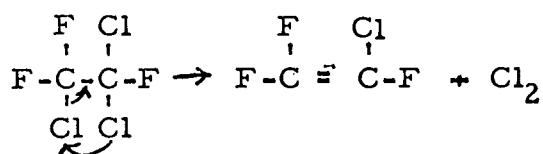
     2.   Free radical formation as:

Initiation $\underset{\underset{Cl\ \ \ Cl}{|\ \ \ \ |}}{\overset{\overset{F\ \ \ Cl}{|\ \ \ \ |}}{F-C-C-F}} \rightarrow \underset{\underset{Cl}{|}}{\overset{\overset{F\ \ \ Cl}{|\ \ \ \ |}}{F-C-C-F}} + Cl\cdot$

Propagation $\underset{\underset{Cl}{|}}{\overset{\overset{F\ \ \ Cl}{|\ \ \ \ |}}{F-C-C-F}} \rightarrow \overset{\overset{F\ \ \ Cl}{|\ \ \ |}}{F-C = C-F} + Cl\cdot$

Termination $2\left[\underset{\underset{Cl}{|}}{\overset{\overset{F\ \ \ Cl}{|\ \ \ \ |}}{F-C-C-F}}\right] \rightarrow \overset{\overset{F\ \ \ Cl}{|\ \ \ |}}{F-C = C-F} + \underset{\underset{Cl\ \ Cl}{|\ \ \ |}}{\overset{\overset{F\ \ \ Cl}{|\ \ \ |}}{F-C-C-F}}$
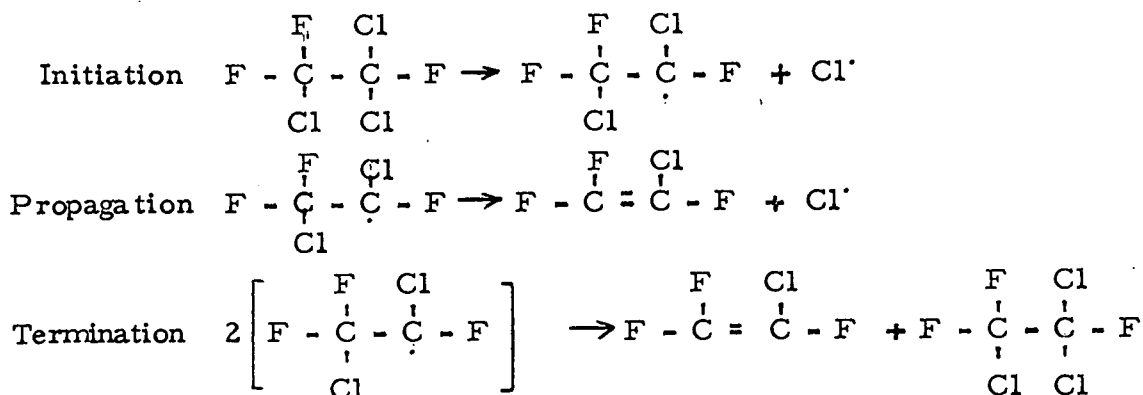
The latter mechanism does not require a coplaner arrangement of four
atoms as the former does, and allows rearrangements to occur on the
free radicals. Several other mechanisms could be postulated, especially
if catalysts and/or other reactants are considered. Distinguishing the
causitive mechanisms would involve many experiments involving various
isomers and pressure-temperature effects. For example, if it could be
demonstrated that $\underset{\underset{}{}}{\overset{\overset{Cl\ \ \ Cl}{|\ \ \ |}}{F - C = C - F}}$ were converted to $F - C \equiv C - F$
while $\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{F - C = C - F}}$ was not, then the free radical mechanism would
seem unlikely. While these conversion processes would be of academic
interest, the establishment of the mechanisms experienced would probably

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contribute little to the purpose of this program except as a predictive aid for original adsorbate concentration. Both charcoal and heat are necessary components of this conversion, since no changes have been noted in the presence of one without the other.

In order to compare the differences in the desorption products between compounds that have been adsorbed over a long period of time and compounds that have been introduced all at once, a Sage Infusion Apparatus with a 5 μ1 syringe was assembled to provide an economical supply of Freon 113 in a carrier gas at ppm levels. This unit delivers 0. 33 μ 1/hr. into an oxygen stream flowing at 30 cc/min. Calculations indicate that such a combination should result in a Freon 113 content of 35 ppm. The stream is split through a tee and each half directed through an adsorption column. Individual flows are controlled by a needle valve located at the head of each adsorption column. Because of some concern over possible losses past the syringe plunger and around the needle during slow injection rates, two test runs were performed. In the first, one microliter of Freon 113 was injected rapidly through the system. Nitrogen was substituted as the carrier gas and the adsorption tubes were replaced with a cryogenic trap. A second 1 μ 1 sample was then introduced through the same system over a period of 3 hours, and the sample trapped in a second cryogenic trap. A comparison of the Freon trapped indicated a large loss through the syringe. However, a replacement syringe in a duplicate test suffered very little or no loss during the 3 hours injection. This system was used to provide the Freon contaminated gas.

The charcoal adsorption tubes were 4 inch lengths of 1/2 inch stainless steel tubing. With a glass wool plug in either end serving as retainers, these tubes would hold approximately 4 grams of charcoal. Swagelock fittings were used to connect them to 1/4 inch tubing for gas flow.

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Freon was adsorbed on charcoal in the adsorption tubes using an oxygen carrier. This charcoal was transferred to the vacuum rack and desorbed without heating. A small quantity of Freon 113 was desorbed. The same sample then was desorbed using heat and vacuum. This desorbate consisted of large quantities of Freon 113 plus chlorotrifluoroethylene, with trace amounts of dichlorodifluoroethylene. This experiment was repeated with elimination of the cold vacuum strip. The results were as before, i. e., large quantities of Freon 113 and chlorotrifluoroethylene, with lesser quantity of dichlorodifluoroethylene.

A 1 μl sample of Freon 113 was added directly to 4 g. charcoal and immediately thermal-vacuum desorbed. The results were the same as noted with the oxygen carrier and slow adsorption.

To investigate the effect of sample size and dwell time on the charcoal, 300 μl were directly added to 4 g. of charcoal. Immediate cold vacuum desorption produced only Freon 113. This sample was sealed under vacuum and stored at room temperature for 72 hours. Cold vacuum stripping again produced only Freon 113. The sample was then heated and vacuum desorbed. The quantity of chlorotrifluoroethylene recovered overloaded the detector system so that desorbates other than Freon 113 could not be determined.

Duplicate experiments were run in which Freon 113 without charcoal was maintained at the stripping temperature for one hour, then was moved through the vacuum system as a desorbate. These samples showed no decomposition.

Freon 113 was added to a sample of firebrick and followed by thermal-vacuum stripping, again no evidence of decomposition or conversion was observed.

This group of experiments conclusively suggests that Freon 113 undergoes significant conversion (over 50% during some of these

tests) to chlorotrifluoroethylene and to a much lesser extent to dichloro-difluoroethylene when exposed to both charcoal and heat, but not to either singly. It could be argued that a fraction of the Freon 113 is very tightly bound and this fraction decomposes at room temperature to yield CTFE which is also tightly bound and does not desorb until heated strongly. However, this argument is refuted by the observations that CTFE is much more volatile than Freon 113 and would be expected to be held much less strongly. A series of tests was run in which up to 20 μl of Freon 113 was adsorbed on 4 g. of charcoal and thermally-vacuum stripped in an effort to resolve the destiny of the chlorine atoms that were removed in the formation of CTFE.

No Cl_2, HCl, or other chlorinated compounds, other than $CFCl = CF_2$ were found in any significant quantities in the trapped (in LN_2) gas phase. The indications are that the chlorine remained on the charcoal as water soluble chloride ions. Quite logically it is expected that any free halogen evolved is immediately reduced to ionic form on the active sites of the charcoal. In dealing with small amounts of sample and adsorbent, there is always a degree of uncertainty but the experimental data has been quite consistent. Table 3 shows the results of these tests. The first 2 columns show the compound and quantity of material added to 4 g. of charcoal.

The amount of Cl^- in 4 g. of charcoal that was extractable in H_2O and total Cl obtained upon combustion of the charcoal with the added compound before the charcoal was stripped is represented by "before stripping." Chlorides remaining on the charcoal after thermal-vacuum treatment are indicated as "after stripping." Finally, the amount of chlorine/chlorides that were collected in liquid nitrogen traps during desorption (vacuum-thermal stripping) is shown in the last column. This material was titratable as chloride ions representing either HCl or chlorine.

Chlorine recoveries indicate an order of magnitude of 50% conversion of Freon 113 and methyl chloroform to other compounds. This consistent with previous GC data. The total chlorine content of the charcoal is essentially equal to the water extractable chlorine content. This indicates that no significant amount of organic chlorides remained adsorbed on the charcoal.

Experiments were done with the adsorption and desorption of Freon 113 as a function of the amount adsorbed and of the time adsorbed on the charcoal. One set of experiments were performed in which 1, 10, 100, and 500 μl of Freon 113 were put on 4 g. of charcoal and thermal-vacuum stripped immediately. Fractions of the desorbed gas were analyzed by gas chromatography for relative amounts of Freon 113 and the major decomposition product, chlorotrifluoroethylene. A second set of samples was stripped after two days of being on the charcoal. The results are summarized in Table 4. The conclusion is that the amount (mass) of chlorotrifluoroethylene produced is independent of the amount of Freon 113 or the residence time on the charcoal. Several assumptions drawn from these data are as follows:

a. Conversion occurs only during the stripping process.

b. The bulk of the Freon 113 is stripped before decomposition occurs.

c. Only the most tightly bound molecules located within the "hot zone" or bound within micropores for some time decompose.

E. QUANTITATIVE RESULTS OF DECOMPOSITION EXPERIMENTS

Rather than further concentrating investigative efforts in determining how and why compound conversion on charcoal occurs, a direct approach was taken to determine what conversion occurs with known compounds. This approach provided data immediately applicable for the correction of previously reported Apollo canister data.

One microliter of sample was added to an evacuated glass flask containing 4 g. of charcoal. Exposure time was varied, but no appreciable differences were noted in the extent of conversion or of compounds formed with exposure time variances of minutes to several days. The flask was then attached to the vacuum rack and the charcoal vacuum-thermally desorbed, using the same temperature program established for and used on Apollo canister study. The same charcoal sample was recycled many times with various compounds without indication of differences in reactivity from fresh charcoal.

Most reactive compounds added to charcoal appear to undergo some decomposition upon vacuum-thermal desorption. Generally, the n-paraffins are least affected and with increasing substitution, unsaturation, and functionality, conversion or decomposition increases in a manner closely resembling thermal degradation fragmentation.

The direct addition of selected compounds to charcoal followed by desorption has been performed as a screening operation. Data reduction has consisted of peak area approximation only with no response corrections and therefore should be considered semi-quantitative. Propane, isoprene, acetylene, ethylene, benzene, toluene, and xylene were found not to react on charcoal under the conditions of the desorption. These results are consistent with the general stability of hydrocarbons.

Tetrahydrofuran - there is an apparent dehydrogenation of approximately 20% of the sample to furan.

Equation: $THF \rightarrow 0.8\ THF + 0.2\ Furan$
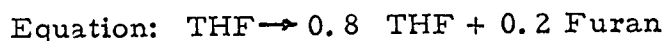
Ethanol - the conversions experienced with ethyl alcohol do not seem to be products of a single mechanism since this material appears to undergo both scission and oxidation.

Equation: EtOH $\rightarrow$ 0. 95 EtOH + 0. 03 MeOH + 0. 02 Acetone

Beilstein (Reference 5) – Ethyl alcohol is claimed to be only slightly decomposed at 700°C in hard glass containers. In metal containers it decomposes at 250°C – 350°C, at 25 atmospheres of pressure into acetaldehyde, ethyl acetate, ethylene, methane, ethane, CO, CO_2, and hydrogen.

Acetone – yields about 20% ethanol.

Equation: Acetone $\rightarrow$ 0. 8 Acetone + 0. 2 EtOH

Beilstein – Acetone is stated to be fairly stable without a catalyst. On aluminum silicate, however, it decomposes at 170°-260°C to isobutylene and acetaldehyde while at 350°C it decomposes to isobutylene, acetic acid, and other products.

Ethyl Acetate – yields 30% ethanol and 10% methanol.

Equation: EtOAc $\rightarrow$ 0. 6 EtOAc + 0. 3 EtOH + 0. 1 MeOH

Isopropanol – decomposes to acetone and propylene.

Equation: iPrOH $\rightarrow$ 0. 8 iPrOH + 0. 15 Acetone + 0. 05 C_3H_6

Beilstein – Isopropanol decomposes to propylene and water at 105 – 110°C, on $NaHSO_4$. It decomposes at 400°C on unglazed clay fragments. Other products that have been isolated from various catalysts are acetone, propylene, methyl isobutyl ketone, diisobutyl ketone, mesitylene oxide, propane, 2-methylpentane, 2-methylpentene, and 2-methylpentadiene.

Butanol – the butanols are found to dehydrate fairly easily to a mixture of butenes.

Equation: Butanol $\rightarrow$ 0. 7 Butanol + 0. 3 Butene

Beilstein – Normal butanol is reported to decompose at 530°C to butene-1 and butyraldehyde, at 600°C to butadiene and at 650°C to benzene, ethylene and cyclopentadiene.

Over nickel-copper catalyst at 224-257°C it decomposes to propane and propylene.

2-Butanol is reported to decompose at 350°-400°C to methyl ethyl ketone, at 450°C to 2-butene, at 600°C to butadiene, acetone and ketene, and at 650°C to benzene, cyclopentadiene, toluene, m-xylene.

At 150°-250°C over copper catalyst it decomposes to methyl ethyl ketone.

Isobutanol decomposes to a mixture of butenes, iso-butylene, and isobutyraldehyde.

Tertiary butanol decomposes to isobutylene and water.

Methyl ethyl ketone - appears to yield a mixture of acetone and butanol.

Equation: 0.8 MEK + 0.1 acetone + 0.1 butanol

Beilstein - Methyl ethyl ketone decomposes to ketene and methyl ketene while at 580°C it yields also CO, methane, and ethylene. With an aluminum silicate catalyst it yields, at 250°C, acetic acid and 3 methyl pentene-2 while propionic acid and 2 methyl butene-1 are products at 400°C.

Freon 113 - on numerous tests has decomposed to yield an average of 20% chlorotrifluoroethylene and 1% dichlorodifluoroethylene.

Equation: F-113 $\rightarrow$ 0.8 F113 + 0.2 C_2F_3Cl + 0.01 $C_2F_2Cl_2$

Table 5 is a summary of the above decomposition reactions.

F. NUMERICAL CORRECTIONS TO PREVIOUS ADSORPTION DATA

1.   Rationale for Development of Equations.

The previous experimental work in this program has shown that many compounds decompose to some extent when adsorbed and then stripped from activated charcoal.   It is desired to develop a method to calculate the composition of the initial adsorbate, given the composition of the desorbate.   The problem is mathematically most tractable if it is assumed that each compound undergoes a fixed percentage decomposition to definite fixed ratios of products, independent of the amount of other constituents present.   This assumption is true in the case of a decomposition reaction of first order in the decomposing species and the time of contact with the charcoal is held constant.   Stating this in another form, the implication is that all occupied sites offer the same amount of decomposition whether they have high, low, or similar heats of adsorption, assuming that the adsorbate concentration is limited to probably 5 mg. per g. of charcoal.   A converse set of plausible assumptions would be:

a.   There are sites of widely differing adsorption energies on the charcoal.

b.   The sites of low energy are emptied so rapidly in the stripping process that no significant decomposition occurs.

c.   Most of the decomposition occurs to the molecules held to the high energy sites.

This set of assumptions would eventually yield a fixed amount and type of desorbate (dependent upon the same adsorbent) independent of the amount of adsorbate.   This extreme would result in simple correction equations.   One would simply find that a constant weight of decomposition products occurred.   This is apparently the case for large amounts of Freon 113, as discussed at the end of Section D.   However, for small amounts, the reaction must approach 1st order.

2.   Development of Equations.

Assume for the first case that we have a set of n equations of
the form

$$C_i \rightarrow \sum_{j=1}^{n} D_{ji} C_j$$

where n is the total number of compounds

$i = 1, n;\ j = 1, n.$ This notation is meant to signify that compound 1, C_1,
decomposes into D_{11} parts of C_1, D_{21} parts of C_2, $\ldots$, D_{n1} parts of C_n.
Similarly compound 2, C_2, decomposes into D_{12} parts C_1, D_{22} parts C_2, $\ldots$,
etc. Let c_i = the observed amount of compound i and c_i^o = the initial amount
of compound i before decomposition. Then we have the simultaneous set of
equations $c_i = \sum_{j=1}^{n} D_{ij}\ c_j^o$ to be solved for c_j^o.

3.   Solution of Equations.

The solution of these equations is fairly straightforward, but
tedious for hand calculation for more than a few components. Consider a
very simple case in which one compound, E, decomposes 10% on charcoal
into compound A, while compound A, if originally present, has decomposed
20% into compound E. In otherwords, they have partially approached an
equilibrium. A third component X doesn't further decompose. Assume
that 3.1 mg. of compound E, 1.9 mg. of compound A, and 5 mg. of com-
pound X have been found. What were the original amounts of compounds

E, A, and X before the decomposition? Let e^o and e represent the original and final amounts of compound E with a similar notation for compounds A and X.

The following equations then express the decomposition:

1. $E \longrightarrow .9 E + .1 A + 0X$

2. $A \longrightarrow .2 E + .8 A + 0X$

3. $X \longrightarrow 0 E + 0 A + 1X$

or the equations to be solved for e^o, a^o, and x^o

4. $e = .9e^o + .2a^o + 0x^o = 3.1$

5. $a = .1e^o + .8a^o + 0x^o = 1.9$

6. $x = 0e^o + 0a^o + 1x^o = 5$

The solution to these simultaneous equations is:

$$e^o = 3, \quad a^o = 2, \quad x^o = 5.$$

In matrix notation, which is well adapted to computer solution, we can represent equations 1, 2, and 3 as column vectors $\begin{pmatrix} .9 \\ .1 \\ 0 \end{pmatrix}$, $\begin{pmatrix} .2 \\ .8 \\ 0 \end{pmatrix}$, $\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$. These can be combined to make a square decomposition matrix, D. $D = \begin{pmatrix} .9 & .2 & 0 \\ .1 & .8 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ Let the compounds present before decomposition be a column vector $c^o = \begin{pmatrix} e^o \\ a^o \\ x^o \end{pmatrix}$ and the observed amounts of compounds be the column vector $c = \begin{pmatrix} e \\ a \\ x \end{pmatrix} = \begin{pmatrix} 3.1 \\ 1.9 \\ 5 \end{pmatrix}$,

we have the matrix equation

$$Dc^o = c$$

or, $\begin{pmatrix} .9 & .2 & 0 \\ .1 & .8 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} e^o \\ a^o \\ x^o \end{pmatrix} = \begin{pmatrix} 3.1 \\ 1.9 \\ 5 \end{pmatrix}$

This is the matrix equivalent of $\sum\limits_{j=1}^{n} D_{ij} c_j^o = c_i$.

7. $c^o = D^{-1} c$

where, $D^{-1} c = \begin{pmatrix} .9 & .2 & 0 \\ .1 & .8 & 0 \\ 0 & 0 & 1 \end{pmatrix}^{-1} \begin{pmatrix} 3.1 \\ 1.9 \\ 5 \end{pmatrix} = \begin{pmatrix} 1.143 & -.2857 \\ -.1429 & 1.286 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

$$= \begin{pmatrix} 3 \\ 2 \\ 5 \end{pmatrix}$$

Matrix D and hence D^{-1} can be finally established for any set of compounds as long as the percent decomposition is independent of the amounts of compounds present. Equation 7 is to be solved and involves only D^{-1}, known, and c, measured. If not many compounds decompose, or the amount of decomposition is small, matrix D will have most of its diagonal terms nearly equal to 1 and most of its off-diagonal terms equal to 0. This fact simplifies calculation of the inverse. The dimension of the matrix will be equal to the total number of possible compounds.

Solution to equation 7 may have some negative values on occasion. This is obviously impossible and means that not as much of a compound has been found as was expected from decomposition on charcoal alone. Probably the best thing to do is set negative values to 0. If this occurs too frequently, one or more off-diagonal terms in the "decomposition matrix," D are obviously too large.

Consider the data from the 90 day manned spacelab. Use only equations 1-7 of Table 5 to calculate corrected compositions. An approximate hand solution to the compositions would be as shown in Table 6. Columns 1 and 2 (of Table 6) are 12 actual compounds and their amounts from this sample. Column 3 is the results of applying equation 1 (Table 5) to the estimated amount of Freon 113 in column 9 to get the expected amounts of Freon 113, C_2F_3Cl and $C_2F_2Cl_2$. Note that these are more than the observed amounts for the last 2 compounds and hence they can be assumed to be due to decomposition only.

Column 4 applies equation 3 approximately to acetone. It is assumed that the amounts of acetone from equations 2, 4, and 7 are small compared to the amount that was not formed from decomposition. The calculated amount of ethanol exceeds the observed amount. Ethanol was probably not present in the original sample.

Columns 6-8 finish applying the remaining decomposition equations.

Column 9 is the first estimate of the corrected concentrations.

A computer solution would proceed as follows: Reactions 1-7 are expressed as a matrix (Table 7).

This matrix also includes reactions such as MeOH $\rightarrow$ 1.0 MeOH (i. e., no decomposition) to obtain the right number of dimensions. This matrix is then inverted and column 2 in Table 6 is multiplied by it to get correct values for column 9. Table 8 is the inverse matrix (calculated by computer) for Table 7 and Table 9 is the computer calculation equivalent to column 9 of Table 6. Note that there are several small negative terms which should be set equal to zero.

Table 10 is the complete inverse decomposition matrix for 15 major components that is to be used for the correction of the analytical data obtained in charcoal desorption studies. This is the matrix, D^{-1}, to be used in the solution of Equation 7 above.

The appendix gives a version of a computer program that was used to solve the matrix equations.

III.   CONCLUSIONS

There is definite decomposition of many adsorbates on charcoal when they are stripped by heat. The compounds to be regarded as at least partially due to decomposition are:

Ethane	Methanol
Propane	Acetone
Ethylene	Acetaldehyde
Propylene	Butanol
Butane	Fluorotrichloroethylene
Butene	Dichlorodifluoroethylene
Ethanol	

Traces of benzene and toluene almost always are present even in "clean" charcoal. Large amounts, ($>0.01\,\mu$ g/g. charcoal), except where removed by the correction equations, are probably present in the original adsorbed sample.

It is recommended that the inverse matrix of Table 10 be applied to the results of previous charcoal analyses to correct for the effects of the charcoal desorption. These corrections should be regarded as only approximate, but they represent the best approach available as of this date.

REFERENCES

1. Chemical Analysis of Adsorbates from Breathing Canisters from Pre-Apollo 7 Spacecraft, Aerojet General Corporation, Analytical Chemistry Laboratories, Final Report, No. 3726, March 1969, Contract NAS 9-8872, Job Order No. 3.

2. Chemical Analysis of Adsorbates from Breathing Canisters from Apollo 13 Spacecraft, Aerojet-General Corporation, Analytical Research Laboratories, Report No. 4108, Oct. 1970, Contract NAS 9-8872, Job Order No. 8.

3. Collection and Measurement of Atmospheric Trace Contaminants, Aerojet ElectroSystems Company, Analytical Research Laboratory, Contract No. NAS 1-9814.

4. A Study of Physiochemical Factors Affecting Charcoal Adsorption of Contaminants in Manned Spacecraft Atmosphere, Analytical Research Laboratories, Inc., Final Report, August 1971, Contract NAS 9-11049

5. Beilstein, Handbook der Organischen Chemie.

6. IBM H20-0205-3, "System/360 Scientific Subroutine Package (360A-CM-03X) Version III, Programmer's Manual"

TABLE 1

LIST OF COUMPOUNDS FOUND ON CHARCOAL

	Compt. ID #	Compound	MW
1	38	FREON 11	137.38
2	2	FREON 12	121.00
3	157	FREON 13	104.46
4	513	FREON 21	102.92
5	4	FREON 22	86.50
6	98	FREON 113	187.39
7	3	FREON 114	171.00
8	83	FLUOROFORM	70.02
9	505	TRIFLUOROMETHANE	70.02
10	528	CARBON TETRAFLUORIDE	88.00
11	193	ETHYL FLUORIDE	48.06
12	92	PENTAFLUOROETHANE	120.00
13	532	HEXAFLUOROETHANE	138.01
14	537	VINYL FLUORIDE	46.04
15	512	DIFLUOROETHYLENE	64.04
16	501	TRIFLUOROETHYLENE	82.02
17	500	TETRAFLUOROETHYLENE	100.02
18	545	TRIFLUOROACETONITRILE	95.02
19	515	DIMETHYLDIFLUOROSILANE	96.16
20	506	FLUOROPROPANE	62.09
21	503	TRIFLUOROPROPANE	98.07
22	541	PENTAFLUOROPROPANE	134.05
23	533	HEXAFLUOROPROPANE	152.04
24	550	OCTAFLUOROPROPANE	188.03
25	509	TRIMETHYLFLUOROSILANE	92.20
26	538	TRIFLUOROPROPENE	96.05
27	544	PENTAFLUOROPROPENE	132.03
28	543	HEXAFLUOROPROPENE	150.02
29	542	OCTAFLUOROBUTANE	202.05
30	146	TRIFLUOROBENZENE	132.09
31	147	TETRAFLUOROBENZENE	150.09
32	148	HEXAFLUOROBENZENE	186.09
33	18	CHLOROFORM	119.39
34	24	METHYLENE CHLORIDE	84.94
35	39	CARBON TETRACHLORIDE	153.18
36	72	METHYL CHLORIDE	50.49
37	12	1,1,1-TRICHLOROETHANE	133.42
38	16	1,2-DICHLOROETHANE	98.97
39	17	TRICHLOROETHYLENE	131.40
40	21	TETRACHLOROETHYLENE	165.85
41	105	1,1-DICHLOROETHANE	98.97
42	113	1,1,2-TRICHLOROETHANE	133.41
43	507	CHLOROACETYLENE	60.49
44	517	ETHYL CHLORIDE	64.52

TABLE 1 (Cont.)

Compt. ID #		Compound	MW
45	35	VINYL CHLORIDE	62.50
46	41	VINYLIDENE CHLORIDE	96.95
47	547	3-CHLOROPROPENE	76.53
48	115	PROPYL CHLORIDE	78.54
49	120	TETRACHLOROETHANE	167.85
50	27	MONOCHLOROBENZENE	112.56
51	153	DICHLOROBENZENE	147.01
52	196	TETRAFLUOROCHLOROETHANE	136.52
53	519	CHLORODIFLUOROETHANE	100.50
54	523	DICHLORODIFLUOROETHANE	134.94
55	502	TRIFLUOROCHLOROETHYLENE	116.48
56	504	FLUOROCHLOROETHYLENE	80.50
57	508	DICHLORODIFLUOROETHYLENE	132.94
58	529	CHLORODIFLUOROETHYLENE	98.50
59	71	METHANE	16.04
60	52	ETHANE	30.07
61	74	PROPANE	44.09
62	65	BUTANE	58.12
63	70	ISOBUTANE	58.12
64	5	PENTANE	72.15
65	54	ISOPENTANE	72.15
66	144	DIMETHYL PROPANE	86.18
67	33	HEXANE	86.17
68	97	2-METHYLPENTANE	72.15
69	197	3-METHYLPENTANE	86.18
70	44	DIMETHYLBUTANE	86.17
71	96	2,2-DIMETHYLBUTANE	86.17
72	10	N-HEPTANE	100.20
73	139	2,4-DIMETHYLPENTANE	100.21
74	154	2,3-DIMETHYLPENTANE	100.21
75	195	DIMETHYLPENTANE	100.21
76	149	TRIMETHYLBUTANE	100.21
77	87	N-OCTANE	114.23
78	47	ISO-OCTANE	114.23
79	143	2,3,4-TRIMETHYL PENTANE	114.23
80	163	N-NONANE	128.26
81	138	TRIMETHYLHEXANE	128.26
82	169	2,2,5-TRIMETHYLHEXANE	128.26
83	110	DECANE	142.29
84	64	ACETYLENE	26.04
85	92	ETHYLENE	28.05
86	69	PROPYLENE	42.08
87	94	PROPADIENE	40.06
88	178	METHYLACETYLENE	40.07
89	549	ETHYL ACETYLENE	54.09
90	66	1-BUTENE	56.10
91	67	2-BUTENE (CIS)	56.10
92	68	2-BUTENE (TRANS)	56.10
93	80	1,3-BUTADIENE	54.09
94	93	ISOBUTYLENE	56.10
95	63	1-PENTENE	70.13

TABLE 1 (Cont.)

	Compt. ID #	Compound	MW
96	510	2-PENTENE	70.13
97	123	CYCLOPENTENE	68.11
98	171	2-METHYL-2-BUTENE	70.13
99	55	ISOPRENE	68.11
100	126	HEXENE	84.16
101	194	2-HEXENE	84.16
102	58	CYCLOHEXENE	82.14
103	160	2-METHYL-1-PENTENE	84.16
104	170	2-METHYL-2-PENTENE	84.16
105	164	2-ETHYL-1-BUTENE	84.16
106	76	N-HEPTENE	98.18
107	166	3-HEPTENE	98.18
108	73	METHYLCYCLOHEXENE	96.17
109	162	2-OCTENE	112.21
110	183	OCTYNE	110.20
111	140	ALPHA-DIISOBUTYLENE	110.20
112	161	2,4,4-TRIMETHYL PENTENE	112.21
113	48	STYRENE	104.14
114	81	CYCLOPROPANE	42.08
115	159	CYCLOPENTANE	70.13
116	23	CYCLOHEXANE	84.16
117	128	METHYLCYCLOPENTANE	84.11
118	43	DIMETHYLCYCLOPENTANE	98.18
119	56	METHYLCYCLOHEXANE	98.18
120	45	DIMETHYLCYCLOHEXANE	112.21
121	167	ETHYLCYCLOHEXANE	112.22
122	155	1,2-DIMETHYLCYCLOHEXANE (CIS)	112.22
123	156	1,2-DIMETHYLCYCLOHEXANE (TR)	112.22
124	88	DECALIN	138.25
125	101	DECALIN ISOMERS	138.25
126	14	BENZENE	78.11
127	20	TOLUENE	92.13
128	22	M-XYLENE	106.16
129	28	O-XYLENE	106.16
130	29	P-XYLENE	106.16
131	82	ETHYLBENZENE	106.16
132	191	C9 AROMATICS	120.19
133	51	TRIMETHYLBENZENE	120.19
134	100	MESITYLENE	120.19
135	135	METHYLETHYLBENZENE	120.20
136	46	INDENE	116.15
137	145	N-PROPYLBENZENE	120.20
138	150	CUMENE	120.20
139	190	C10 AROMATICS	134.21
140	50	TETRAMETHYLBENZENE	134.21
141	119	DIETHYLBENZENE	134.21
142	157	ISOPROPYLTOLUENE	134.21
143	40	NAPHTHALENE	128.16
144	121	T-BUTYLBENZENE	134.21
145	151	N-BUTYL BENZENE	134.21
146	152	SEC-BUTYLBENZENE	134.21

TABLE 1 (Cont.)

	Compt. ID #	Compound	MW
147	534	C11 AROMATICS	148.24
148	53	METHYLNAPHTHALENE	142.19
149	42	DIMETHYLNAPHTHALENE	156.22
150	189	TERT. GROUP C14 AROM.	184.00
151	61	FURAN	68.07
152	118	FURFURAL"	96.08
153	57	TETRAHYDROFURAN	72.10
154	59	DIOXANE	88.10
155	49	METHYLFURAN	82.10
156	77	DIMETHYLFURAN	96.12
157	536	DIBENZOFURAN	168.18
158	141	INDOLE	117.15
159	78	SKATOLE	131.17
160	13	METHYL ALCOHOL	32.04
161	15	ETHYL ALCOHOL	46.07
162	553	ETHYLENE GLYCOL	62.07
163	37	ALLYL ALCOHOL	58.08
164	75	N-PROPYL ALCOHOL	60.09
165	25	ISOPROPYL ALCOHOL	60.09
166	30	N-BUTYL ALCOHOL	74.12
167	173	T-BUTYL ALCOHOL	74.12
168	174	SEC-BUTYL ALCOHOL	74.12
169	26	ISOBUTYL ALCOHOL	74.12
170	525	ETHYL CELLOSOLVE	90.12
171	109	N-AMYL ALCOHOL	88.15
172	125	FURFURYL ALCOHOL	98.10
173	181	ISOAMYL ALCOHOL	88.15
174	552	3-METHYLBUTANOL-2	88.15
175	535	PHENOL	94.11
176	158	CYCLOHEXYL ALCOHOL	134.21
177	168	2-HEXYL ALCOHOL	102.18
178	184	CAPRYL ALCOHOL	130.23
179	520	2-ETHYLBUTYL ALCOHOL	102.17
180	521	2-ETHYLHEXYL ALCOHOL	130.23
181	554	HYDROXYQUINOLINE	145.15
182	8	ACETONE	58.08
183	11	METHYL ETHYL KETONE	72.10
184	192	METHYL PROPYL KETONE	86.13
185	117	2-METHYL-3-BUTANONE	86.13
186	165	ACETYL ACETONE	100.11
187	19	METHYL ISOBUTYL KETONE	100.16
188	177	CYCLOHEXANONE	98.14
189	526	ACETOPHENONE	120.14
190	548	ETHYLENE OXIDE	44.05
191	187	DIMETHYL ETHER	46.07
192	6	DIETHYL ETHER	74.12
193	34	ISOPROPYL ETHER	102.17
194	555	METHYLISOPROPYL ETHER	74.12
195	91	DIMETHOXYBENZENE	138.16
196	102	BENZYL ETHER	198.25
197	31	ACETALDEHYDE	44.05

TABLE 1 (Cont.)

	Compt. ID #	Compound	MW
198	518	ACROLEIN	56.06
199	522	PROPIONALDEHYDE	58.08
200	79	BUTYRALDEHYDE	72.10
201	179	CROTONALDEHYDE	70.09
202	175	BENZALDEHYDE	106.12
203	9	METHYL ACETATE	74.08
204	84	ETHYL FORMATE	74.08
205	32	ETHYL ACETATE	88.10
206	527	METHYL LACTATE	104.11
207	36	PROPYL ACETATE	102.13
208	86	METHYL-N-BUTYRATE	102.13
209	108	METHYL METHACRYLATE	100.12
210	127	ISOPROPYL ACETATE	102.13
211	516	ETHYL LACTATE	118.13
212	90	BUTYL ACETATE	116.16
213	111	ISOBUTYL ACETATE	116.16
214	524	CELLOSOLVE ACETATE	132.16
215	112	AMYL ACETATE	130.18
216	514	BUTYL LACTATE	146.19
217	539	PHTHALATE ESTER	0.00
218	182	ACETONITRILE	41.05
219	89	ACETIC ACID	60.05
220	180	METHOXYACETIC ACID	90.08
221	186	ACRYLIC ACID	72.06
222	103	PROPIONIC ACID	74.08
223	99	VALERIC ACID	102.13
224	85	METHYL AMINE	31.06
225	124	DIMETHYL AMINE	45.08
226	172	T-BUTYL AMINE	73.14
227	116	METHYL MERCAPTAN	48.11
228	122	CARBON DISULFIDE	76.14
229	530	CARBON OXYSULFIDE	60.07
230	60	DIMETHYL SULFIDE	62.13
231	546	DIMETHYLDISULFIDE	94.20
232	114	ETHYL MERCAPTAN	62.13
233	104	PROPYL MERCAPTAN	76.15
234	134	THIOPHENE	84.14
235	511	DIETHYL SULFIDE	90.11
236	132	METHYLTHIOPHENE	98.17
237	138	DIMETHYLTHIOPHENE	112.19
238	131	METHYLETHYLTHIOPHENE	126.18
239	1	CARBON DIOXIDE	44.00
240	106	HYDROGEN FLUORIDE	20.01
241	107	HYDROGEN SULFIDE	34.08
242	129	NITROUS OXIDE	44.01
243	130	HYDROGEN	2.02
244	185	NITROMETHANE	61.04
245	188	SILICONE SI-R	0.00
246	531	SULFUR DIOXIDE	64.06

TABLE 2

ELEMENTAL ANALYSIS OF AC CHARCOAL

Element	Platinum Crucible	Gold Crucible
Boron	trace	trace
Silicone	major	major
Manganese	trace	trace
Potassium	moderate	moderate
Antimony	trace	trace
Gold	N. D.	trace
Magnesium	moderate	moderate
Iron	moderate	moderate
Aluminum	major	major
Vanadium	trace	trace
Calcium	minor	minor
Sodium	moderate	moderate
Titanium	minor	minor
Copper	trace	trace
Nickel	trace	trace
Zinc	N. D.	N. D.
Tungsten	N. D.	N. D.
Platinum	N. D.	N. D.
Silver	N. D.	N. D.
Chromium	N. D.	N. D.
Lithium	N. D.	N. D.
Tin	N. D.	N. D.
Lead	N. D.	N. D.

Trace	< 0.01%
Minor	0.01 - 0.1%
Moderate	0.1 - 1.0%
Major	> 10%

TABLE 3

ANALYSIS OF CHARCOAL SAMPLES FOR CHLORINE

Compound Tested	Amount used, μm.*	Charcoal before vacuum stripping μ.m.		Charcoal after vacuum stripping μm.		Collected by desorption, m
		Water Soluble	Total Cl⁻	Water Soluble	Total Cl⁻	Total Cl⁻
Blank	-	83	80	-	-	-
Methyl Chloroform	50	87	226	180	171	.4
Freon 113	42	78	131	118	98	.5
HCl (36% acid)	58	75	72	75	67	.8
Blank	-	-	-	137	-	1.6
Methyl Chloroform	202	-	-	343	-	-
Freon 113	167	-	-	274	-	-
HCl (36% acid)	232	-	-	274	-	-

μm = micromoles

TABLE 4

Effect of Time of Residence and of Concentration of Freon 113

on the Amount of Decomposition of Freon 113

Adsorbed on 4 g of Charcoal

Amount Freon 113 Introduced, mg	Length of Stay days	Fraction of Total Sample Analyzed	Amount Freon 113 Recovered, mg	Amount ClFCCF$_2$ Recovered, mg	Ratio F113/ClFCCF$_2$
500	0	$\frac{1}{1013}$	300	.107	2800
620	2	$\frac{1}{974}$	228	.108	2100
95	0	$\frac{1}{195}$	76	0.03	2200
97	2	$\frac{1}{203}$	5.9	0.22	26
10	0	$\frac{1}{20}$	4.9	3.2	1.5
10	0	$\frac{1}{20}$	0.76	1.1	.68
9.6	2	$\frac{1}{188}$	0.2	.567	.36
1	0	$\frac{1}{31}$	0.1	0.4	0.25
1	2	$\frac{1}{20}$	0.28	0.05	5.4

TABLE 5

APPROXIMATE VALUES OF DECOMPOSITION COEFFICIENTS

1.	Freon 113	0.8 F113 $+ 0.2$ C_2F_3Cl $+ 0.01$ $C_2F_2Cl_2$
2.	Ethanol	$.95$ EtOH $+ 0.03$ MeOH $+ 0.02$ acetone
3.	Acetone	0.8 acetone $+ 0.2$ EtOH
4.	Methyl Ethyl ketone	0.8 Mek $+ 0.1$ acetone $+ 0.1$ butanol
5.	Ethyl Acetate	0.6 EtAc $+ 0.3$ EtOH $+ 0.1$ Methanol
6.	Methyl Iso-butyl ketone	0.5 MIBK $+ 0.5$ C_3H_6
7.	Isopropanol	0.8 Isopropanol $+ 0.15$ acetone $+ 0.05$ C_3H_6
8.	THF	0.8 THF $+ 0.2$ Furan
9.	Butanol	0.7 Butanol $+ 0.3$ Butene

TABLE 6

APPROXIMATE SOLUTION OF ONE SET OF
90-DAY MANNED SPACELAB TESTS

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
(1)	Freon 113	.22	.22						.27
(2)	C_2F_3Cl	.0043	.05						0
(3)	$C_2F_2Cl_2$	.00051	.002						0
(4)	Ethanol	.0078		.08		.004			0
(5)	Ethyl Acetate	.0083				.008			.014
(6)	Methanol	.0042				.001			.003
(7)	Acetone	.32		.32	.0022			.0015	.4
(8)	Isopropanol	.008						.01	.01
(9)	Butanol	.00024			.0022				0
(10)	Methyl ethyl ketone	.018			.018				.022
(11)	Methyl ethyl iso-butyl ketone	.0051					.01		.01
(12)	Propane	.0043					.01		0

TABLE 7

DECOMPOSITION MATRIX FOR TABLE 5

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
) Freon 113	.8											
) C_2F_3Cl	.2	1										
·) $C_2F_2Cl_2$	.01		1									
) Ethanol				.95	.3		.2					
) Ethyl acetate					.6							
·) Methanol				.03	.1	1						
) Acetone				.02			.8	.15		.1		
) Isopropanol								.8				
) Butanol									1	.1		
·) Methyl ethyl ketone										.8		
) Methyl iso-butyl ketone											.5	
) Propane								.05			..5	1

TABLE 8

INVERSE DECOMPOSITION MATRIX FOR 12 COMPOUNDS

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1) Freon 113	1.25											
2) C_2F_3Cl	-0.25	1.0										
3) $C_2F_2Cl_2$	-0.01		1.0									
4) Ethanol				1.06	-0.53		-0.26	0.05		0.03		
5) Ethyl acetate					1.67							
6) Methanol				-0.03	-0.15	1.0	0.01					
7) Acetone				-0.03	0.01		1.26	-0.24		-0.16		
8) Isopropanol								1.25				
9) Butanol									1.0	-0.12		
10) Methyl ethyl ketone										1.25		
11) Methyl iso-butyl ketone											2.0	
12) Propane								-0.06			-1.0	1.0

TABLE 9

CALCULATION OF CORRECTED COMPOSITIONS
FOR 90-DAY MANNED SPACELAB

	Compound	Observed Amount	Corrected Amount
1.	Freon 113	0.22	0.275
2.	C_2F_3Cl	0.0043	-0.051
3.	$C_2F_2Cl_2$	0.00051	-0.002
4.	Ethanol	0.0078	-0.080
5.	Ethyl acetate	0.0083	0.014
6.	Methanol	0.0042	0.005
7.	Acetone	0.32	0.397
8.	Isopropanol	0.008	0.010
9.	Butanol	0.00024	-0.002
10.	Methyl ethyl ketone	0.018	0.023
11.	Methyl isobutyl ketone	0.0051	0.010
12.	Propane	0.0043	-0.001

TABLE 10

INVERSE DECOMPOSITION MATRIX FOR 15 COMPOUNDS

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
(1)	1.25														
(2)	-0.25	1.0													
(3)	-0.01		1.0												
(4)				1.06	-0.53		-0.26	0.05		0.03					
(5)					1.67										
(6)				-0.03	-0.15	1.0	0.01								
(7)				-0.03	0.01		1.26	-0.24		-0.16					
(8)								1.25							
(9)									1.43	-0.18					
(10)										1.25					
(11)											2.0				
(12)								-0.06		-1.0	1.0				
(13)													1.25		
(14)													-0.25	1.0	
(15)									-0.43	0.05					1.0

The rows and columns correspond to these compounds:

- (1)   Freon 113
- (2) C_2F_3Cl
- (3) $C_2F_2Cl_2$
- (4)   Ethanol
- (5)   Ethyl acetate
- (6)   Methanol
- (7)   Acetone
- (8)   Isopropanol
- (9)   Butanol
- (10)   Methyl ethyl ketone
- (11)   Methyl isobutyl ketone
- (12)   Propane
- (13)   Tetrahydrofuran
- (14)   Furan
- (15)   Butene

APPENDIX

Presented in this appendix is the listing of the program used for the solution of the matrix equations derived in Section F of the Technical Discussion. This is intended to be a sample program only. The program is dimensioned for 12x12 matrices and the dimensions have to be changed accordingly from larger matrices. The major part of the program consists of the IBM LLSQ Scientific Subroutine with the first page added to control input and output. This portion needs to be rewritten according to the desired output. The input consists of matrix A (the decomposition matrix) and the vector B, the amount of each compound present. Matrices AT and BT are working areas, as well as vectors AUX and IPIV.

For matrices of dimension N where N is different from 12, all values of 12 on the first page should be replaced by the value of N. Matrix AUX should be dimensioned 2N.

Subroutine LLSQ is a useful general purpose routine to solve matrix equations of the form $Bj - AXj = min$; A is an $m \times m$ matrix($m \geq n$), B is an $m \times d$ matrix, and X is an $n \times 1$ matrix. In other words, it will give a least squares solution to an over-determined system of linear equations. If one has a set of m unknowns and n equations where $m > n$, there is generally no solution for the m unknowns but there is a set of values which will make the sum of the squares of the residuals of the n equations a minimum. When $m = n$, the solution is equivalent to the solution of a set of m unknowns in m equations. When $m = n = 1$ and B is the unit matrix, X is the inverse of A. Reference 6 contains a complete description of LLSQ.

The input to this sample program consists of a set of cards in two groups. The first group contains the non-zero terms of the A, one term to a card, matrix in format (2I3, F8.5) with the first two fields containing the i and j values and the third field the value of the component. When both i and j reach 12 the program expects the following 3 cards to contain the values of the B vector, 5 to a card, in format (5F 14.5). The first call to subroutine LLSQ calculates the vector X and the second call calculates A^{-1}.

```
      DIMENSION A(12,12),X(12,12),B(12),AT(12,12),BT(12,12)
     1 ,IPIV (12),AUX(24)
    1 DO 2 I=1,12
      DO 2 J=1,12
      A(I,J)=0.
    2 BT(I,J)=0.
    3 READ(7,50)I,J,A(I,J)
   50 FORMAT(2I3,F8.5)
      IF (I.NE.12.OR.J.NE.12)   GO TO 3
    4 READ(7,51)(B(I),I=1,12)
   51 FORMAT(5F14.5)
      DO 5 I=1,12
      BT(I,1)=B(I)
      DO 5 J=1,12
    5 AT(I,J)=A(I,J)
      WRITE (6,52) ((AT(I,J),J=1,12),I=1,12),(BT(I,1),I=1,12)
   52 FORMAT (1X,12F8.5)
      CALL LLSQ(AT,BT, 12,12,1,X,IPIV,.0001,IER,AUX)
      WRITE (6,54)
      WRITE (6,53) IPIV,IER
      WRITE (6,54)
      WRITE (6,52) ((X(I,J),J=1,12),I=1,12),AUX
   53 FORMAT (12I3)
      WRITE (6,54)
      DO 6 I=1,12
      DO 6 J=1,12
      AT(I,J)=A(I,J)
    6 BT(I,J)=0.
      DO 7 I=1,12
    7 BT(I,I)=1.
      WRITE (6,54)
      WRITE (6,52) ((AT(I,J),J=1,12),I=1,12),((BT(I,J),J=1,12),I=1,12)
   54 FORMAT (1H0)
      WRITE (6,54)
      CALL LLSQ(AT,BT,12,12,12,X,IPIV,.0001,IER,AUX)
      WRITE (6,53) IPIV,IER
      WRITE (6,54)
      WRITE (6,52) ((X(I,J),J=1,12),I=1,12)
      END
```

```
   SUBROUTINE LLSQ (A,B,M,N,L,X,IPIV,EPS,IER,AUX)
   DIMENSION A(1),B(1),X(1),IPIV(1),AUX(1)
   IF(M-N)30,1,1
 1 PIV=0.
   IEND=0.
   DO 4 K=1,N
   IPIV(K)=K
   H=0.
   IST = IEND + 1
   IEND = IEND + M
   DO 2  I = IST, IEND
 2 H= H + A(I) * A (I)
   AUX(K) = H
   IF (H- PIV)4,4,3
 3 PIV = H
   KPIV = K
 4 CONTINUE
   IF (PIV) 31,31,5
 5 SIG = SQRT (PIV)
   TOL = SIG * ABS(EPS)
C
C  DECOMPOSITION LOOP
   LM=L*M
   IST=-M
   DO 21 K=1,N
   IST=IST+M+1
   IEND=IST+M-K
   I=KPIV-K
   IF(I)8,8,6
C
C  INTERCHANGE K-TH COLUMN OF A WITH KPIV-TH IN CASE KPIV.GT.K
 6 H=AUX(K)
   AUX(K)=AUX(KPIV)
   AUX(KPIV)=H
   ID=I*M
   DO 7 I=IST,IEND
   J=I+ID
   H=A(I)
   A(I)=A(J)
 7 A(J)=H
C
```

```
C       COMPUTATION OF PARAMETER SIG
     8  IF(K-1)11,11,9
     9  SIG=0.
        DO 10 I=IST,IEND
    10  SIG=SIG+A(I)*A(I)
        SIG=SQRT(SIG)
C
C       TEST ON SINGULARITY
        IF(SIG-TOL)32,32,11
C
C       GENERATE CORRECT SIGN OF PARAMETER SIG
    11  H=A(IST)
        IF(H)12,13,13
    12  SIG=-SIG
C
C       SAVE INTERCHANGE INFORMATION
    13  IPIV(KPIV)=IPIV(K)
        IPIV(K)=KPIV
C
C       GENERATION OF VECTOR UK IN K-TH COLUMN OF MATRIX A AND OF
C       PARAMETER BETA
        BETA=H+SIG
        A(IST)=BETA
        BETA=1./(SIG*BETA)
        J=N+K
        AUX(J)=-SIG
        IF(K-N)14,19,19
C
C       TRANSFORMATION OF MATRIX A
    14  PIV=0.
        ID=0
        JST=K+1
        KPIV=JST
        DO 18 J=JST,N
        ID=ID+M
        H=0.
        DO 15 I=IST,IEND
        II=I+ID
    15  H=H+A(I)*A(II)
        H=BETA*H
        DO 16 I=IST,IEND
```

```
      II=I+ID
   16 A(II)=A(II)-A(I)*H
C
C     UPDATING OF ELEMENT S(J) STORED IN LOCATION AUX(J)
      II=IST+ID
      H=AUX(J)-A(II)*A(II)
      AUX(J)=H
      IF(H-PIV)18,18,17
   17 PIV=H
      KPIV=J
   18 CONTINUE
C
C     TRANSFORMATION OF RIGHT HAND SIDE MATRIX B
   19 DO 21 J=K,LM,M
      H=0.
      IEND=J+M-K
      II=IST
      DO 20 I=J,IEND
      H=H+A(II)*B(I)
   20 II=II+1
      H=BETA*H
      II=IST
      DO 21 I=J,IEND
      B(I)=B(I)-A(II)*H
   21 II=II+1
C     END OF DECOMPOSITION LOOP
C
C
C     BACK SUBSTITUTION AND BACK INTERCHANGE
      IER=0
      I=N
      LN=L*N
      PIV=1./AUX(2*N)
      DO 22 K=N,LN,N
      X(K)=PIV*B(I)
   22 I=I+M
      IF(N-1)26,26,23
   23 JST=(N-1)*M+N
      DO 25 J=2,N
      JST=JST-M-1
      K=N+N+1-J
```

```
      PIV=1./AUX(K)
      KST=K-N
      ID=IPIV(KST)-KST
      IST=2-J
      DO 25 K=1,L
      H=R(KST)
      IST=IST+N
      IEND=IST+J-2
      II=JST
      DO 24 I=IST,IEND
      II=II+M
   24 H=H-A(II)*X(I)
      I=IST-1
      II=I+ID
      X(I)=X(II)
      X(II)=PIV*H
   25 KST=KST+M
C
C
C     COMPUTATION OF LEAST SQUARES
   26 IST=N+1
      IEND=0
      DO 29 J=1,L
      IEND=IEND+M
      H=0.
      IF(M-N)29,29,27
   27 DO 28 I=IST,IEND
   28 H=H+B(I)*B(I)
      IST=IST+M
   29 AUX(J)=H
      RETURN
C
C     ERROR RETURN IN CASE M LESS THAN N
   30 IER=-2
      RETURN
C
C     ERROR RETURN IN CASE OF ZERO-MATRIX A
   31 IER=-1
      RETURN
C
C     ERROR RETURN IN CASE OF RANK OF MATRIX A LESS THAN N
```

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```
32 IER=K-1
   RETURN
   END
```